CONVERSION OF OXO AND THIOMOLYBDATES
TO ACTIVE DISPERSED CATALYSTS

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ABSTRACT

Oxomolybdates impregnated on coal are excellent catalyst precursors in the liquefaction of Wyodak coal, especially when sulfur is added during the reaction. It has been suggested that the active catalysts are oxothiomolybdates. This paper discusses two approaches toward converting oxomolybdates into active catalysts and identifying the types of Mo-S bonding that contribute toward their activity. In the first, several oxothiomolybdates having different forms of Mo-S bonds were prepared in our laboratory and impregnated onto Wyodak coal. THF dissolution and resid conversion for these precursors were determined both in the presence and absence of added H_2S. In the second approach, ammonium heptamolybdate was treated in flowing H_2S in H_2 at temperatures to permit slow conversion of the oxomolybdate into its active form. The effect of this pretreatment on the activities of these catalyst impregnated coals were determined.

INTRODUCTION

A vast amount of observations has indicated that the presence of sulfur is important to coal liquefaction. For molybdenum based catalyst, it is generally agreed that the predominant active species for the primary coal liquefaction is some form of molybdenum sulfide, e.g., MoS_2. The active species may be produced by the decomposition of molybdenum precursors under liquefaction condition. When metal sulfide catalysts are used, a source of sulfur such as hydrogen sulfide, carbon disulfide, or elemental sulfur is introduced to the reactor to maintain the catalysts in a sulfided form. If the precursor contains no sulfur, external sulfur participates in forming the highly active phase. If excess sulfur is present in a sulfur containing precursor, some must diffuse out to allow transformation into the active phase to occur.[1] The importance of the correct stoichiometry of Mo sulfide has also been emphasized by Montano.[2]

The type of catalyst precursor and its activation conditions are important factors influencing the function of the molybdenum catalyst. Utz et al.[3] compared the effects of ammonium tetrathiomolybdate (ATTM), MoS_3, and ammonium heptamolybdate (AHM) on the liquefaction yields of coals. Two activation methods employed were rapidly heating up the reactor to 450°C in 1-2 minutes and slowly heating up in 45-60 minutes. Their results showed greater activities of ATTM and MoS_3 when they were heated rapidly, while slow heating favored AHM. They suggested that since ATTM and MoS_3 were already in a sulfided form, they could decompose more rapidly to a highly dispersed active phase. The transition of AHM to MoS_2 having a high surface area was slow because an external sulfur source was required. By studying the temperature and pressure profiles in a batch reactor, Bockrath et al.[4] found that the molybdenum sulfide was able to participate in liquefaction reactions at low temperature, e.g., 350°C, in contrast to the conventional 400-465°C. They concluded that the dispersed catalyst should be present in an already active form rather than allowing a precursor to undergo transformation during liquefaction. The influence of catalyst precursor on coal conversion also was investigated by Hirschon and Wilson,[1,5] who used Illinois #6 coal with various molybdenum precursors. They found that much higher toluene solubles could be obtained with organometallic complexes than with aqueous metal salts. They suggested that the higher activity of the molybdenum sulfide complex could be attributed to its better dispersion and already being present in highly active form. Subsequent activation during liquefaction was unnecessary. Our recent studies indicate that low-cost water-soluble oxomolybdate salts can be transformed into liquefaction catalysts having activity comparable to more expensive oil soluble precursors.[6]

Although oxomolybdates have demonstrated substantial activity toward coal liquefaction in the presence of H_2S, we suspect that their transformation into active phase can be achieved in situ. The objective of this study is to investigate approaches for improving the activity of dispersed catalysts generated from oxomolybdates. A series of Mo based compounds with various sulfur content were prepared from H_2S and oxomolybdate before impregnating them on coal. Another approach that was also tested was to pretreat the oxomolybdate impregnated coal slurry with H_2S in H_2 to convert the precursor to oxothiomolybdate prior to reaction. This method has been reported to form an active catalyst or close intermediate to an active species.[7,8]

EXPERIMENTAL

Materials   Elemental analysis of the Black Thunder Wyodak coal are presented in Table 1. The as-received coal was impregnated with an aqueous solution containing various concentrations of catalyst precursors at the level of 0.5 g solution/g coal. The concentration of the aqueous solution was varied so that desired Mo loadings on coal could be achieved. In all of the cases, the coal paste was dried at 125 Torr and 100°C for two days to completely remove water. Solvent used in this study comprised mixtures of heavy distillate and deashed resid from Run 262e made at the Advanced Coal Liquefaction R&D Facilities at Wilsonville, AL. The properties of these materials, which were produced when the plant was operated with the same coal, are also summarized in Table 1. Ammonium heptamolybdate (AHM, Aldrich, A.C.S. reagent) and tetrahydrofuran (THF, Aldrich) were used as received. Ammonium dioxodithiomolybdate (ADOM), ammonium tetrathiomolybdate (ATTM), and three types of ammonium polythiomolybdate having different sulfur contents were prepared in our lab from AHM and H_2S. ATTM was prepared by the method of Naumann and Behan[9], AOTM was prepared by the method of McDonald et al.,[10] APTM-1A and APTM-2A $((NH_4)_2[Mo_2^VS_{12}]\cdot 2H_2O)$ were prepared by the method of Müller and Krickemeyer,[11] and APTM-P $((NH_4)_2\cdot Mo_3S(S_2)_6\cdot 2H_2O)$ was prepared by the method of Kurtak and Hartzog.[12] The compositions of these material are summarized in Table 2. In all experiments, catalyst loadings were reported as mg Mo per kg dry coal.

Catalyst Pretreatment In some of the experiment, the oxomolybdate impregnated coal slurry was pretreated prior to reaction with H_2 containing 8 vol% H_2S. In a typical run, the reactor was loaded with coal slurry and placed horizontally in a furnace after purging with H_2 to remove air. The pretreatment was conducted at 300 psig and a gas flowrate of 200 ml/min (STP). The furnace was heated to 120 °C and held for 30 min after which it was successively heated to 250 and 360 °C while holding for 30 minutes at each temperature. After pretreating at 360 °C, the reactor was cooled, vented and subjected to regular reaction procedures described in the following section.

Coal Liquefaction Reaction Procedures   All of the experiments were conducted in a 65 ml microreactor which was agitated at 400 rpm in a fluidized sand bath (Techne, SBL-2D) maintained at 440°C with an Omega CN4600 temperature controller. In every run, 3 g dry coal, 1.8 g heavy distillate, and 3.6 g deashed resid were added to the reactor which was then pressurized to 1000 psig at room temperature with H_2 containing 3 vol% H_2S. Except in some runs when the reactor was charged with pure H_2 only, all reactions were performed at the above baseline reaction conditions. After 30 minutes reaction time, the reactor was removed and quenched in ice water. The liquid and solid products were scraped from the reactor using THF and subjected to Soxhlet extraction for 18 hours. The THF soluble material was distilled at 1 Torr and an atmospheric equivalent cut point of 566°C according to ASTM method D-1160 . This cut point corresponds to that used in the pilot plant where the solvent was generated. All experiments were replicated at least twice to assure the reproducibility.

THF coal conversion and resid conversion were defined below as a measure of catalyst activity on an maf coal basis.

$$Coal\ Conv.\ =\ 100\times(1-\frac{[IOM]_{product}}{Coal(maf)}) \tag{1}$$

$$Resid\ Conv.\ =\ 100\times(\frac{[Coal(maf)+Resid]_{feed}-[IOM+Resid]_{product}}{Coal(maf)}) \tag{2}$$

RESULTS AND DISCUSSION

Effect of Oxothiomolybdates on Coal Liquefaction In this study, several sulfur containing molybdenum compounds including AOTM, ATTM, and three types of APTM were used as catalyst precursors to examine the effect of sulfur content in precursors on liquefaction. Conversions with these precursors at Mo loading of both 100 and 300 ppm are shown in Figures 1 and 2.

In the presence of H_2S, coal conversion was almost unchanged at both catalyst loadings. However, in the absence of added H_2S, coal conversions increased significantly for precursors having S/Mo ratios $\geq$ 4. Another sizable increase was observed for APTM-1A which contains a S/Mo ratio of 10.9. This material had been extracted with CS_2 to remove free sulfur and probably contained a large fraction of polysulfide bonds. As shown in Figure 2, resid conversion increased slowly as the S/Mo ratio increased, whether in the presence or absence of H_2S. Because of the wide variations observed in the resid conversion values, however, the data do not show a statistically significant difference between precursors having S/Mo ratios from 2 to 6. Overall, the presence of sulfur is important to both coal and resid conversions whether sulfur is supplied externally or is present in the catalyst precursor. Lower conversions observed in the absence of H_2S may be due to insufficient sulfur in the reactor to sulfide the precursors and to protect the active phase from being oxidized by

the water. Since the fraction of converted precursor apparently increased as sulfur increased, coal conversion also increased as the S/Mo ratio in the precursor increased. When H_2S was introduced to the reactor, the amount of sulfur carried in by the precursor became negligible compared to the total sulfur available, thus coal conversion became independent of the S/Mo ratio.

Since coal solubilization takes place very early during liquefaction, without added H_2S, the small amount of sulfur associated with the precursors may be sufficient to transform and stabilize an active phase for a short period. Within that period when conversion is occurring, THF solubilization showed an increase as the S/Mo ratio in the precursor increased. Since resid conversion progresses over a longer period, the active phase may lose sulfur through oxidation by water causing the catalyst to deactivate. Thus, an added source of sulfur is necessary to maintain the catalyst in an active form. Clearly, an external sulfur source is necessary for precursors already containing a significant concentration of sulfur.

In coal liquefaction with impregnated catalyst, it is generally assumed that catalyst precursor converts to sulfided active phase *in situ*. There is evidence showing that the activity of the final catalyst depends upon the conditions employed during its preparation.[7] At high temperatures typical of coal liquefaction, an oxomolybdate catalyst precursor such as AHM experiences two type of competition reactions, i.e., thiosubstitution and decomposition. When the rate of ammonia loss due to decomposition is greater than the rate of thiosubstitution, the intermediate Mo compounds are more difficult to sulfide. Therefore, complete sulfidation of ammonium oxomolybdate by H_2S under liquefaction conditions may not occur. By contrast, in oxothiomolybdates, the loss of ammonia is not critical since the catalysts are already in their sulfided forms. Complete conversion of these precursors to an active catalyst is more likely through reaction with the H_2S or intramolecular rearrangement transfer of the sulfur in precursors. For different sulfur-containing precursors, there may be differences in their decomposition mechanisms and kinetics. The chemical form and the number of active sites may also differ as reflected by the different activities towards resid conversion.

Another factor that affects the formation of active catalyst is the presence of water. Although the impregnated coal was dried before reaction, inevitably, some water will be present in the reactor as a result of deoxygenation reactions. At high temperatures and in the presence of water, the Mo catalyst will deactivate as it gains oxygen from water. Also, water may cause removal of sulfur, thus deactivating the catalyst. The observation that resid conversion increases with the S/Mo ratio in the presence of H_2S may also be attributed to the fact that the oxothiomolybdate catalyst may remain the active phase as excess sulfur is lost in the presence of water.

Pretreatment of oxomolybdate impregnated coal slurry with H_2S/H_2 Sulfur is obviously important for the transformation of these oxo and thiomolybdate precursors into an active catalytic phase. In order to have a better understanding of this transformation, a series of tests were made in which AHM impregnated coal slurries were pretreated with H_2S. In every run, the catalyst impregnated coal was dried, slurried with solvent, and pretreated in a stream of H_2S/H_2 at a series of temperatures at 300 psig.

A blank run was made to determine the effect that pretreating coal for 90 minutes at a sequence of temperatures up to 360°C would have on conversions at 440°C. THF and resid conversions for a coal impregnated with AHM to a Mo loading of 100 ppm were quite small, i.e., 3.6% and 2.4%, respectively. Therefore, conversions observed at 440 °C are not significantly influenced by the 90 minutes pretreatments at ≤ 360°C and 300 psig.

For coals impregnated with 100 and 300 ppm Mo, THF coal conversions were not affected by the pretreatment, as shown in Figure 3. The most noticeable effect is an increase in resid conversion for the coal loaded with 100 ppm Mo. The resulting resid conversion is the same as that achieved with the coal loaded with 300 ppm Mo. This result suggests that the pretreatment converts a large fraction of the precursor to an active phase. At the 300 ppm Mo loading, no apparent advantage was gained from pretreating.

It appears that pretreating the coal slurry with H_2S/H_2 improves resid conversion. Also, high resid conversions can be obtained by using an oversulfided Mo substrate such as APTM-1A. Note that the following two 100 ppm Mo impregnated coals were as active as the 300 ppm Mo impregnated coals.

	Resid Conv, maf coal
100 ppm Mo as AHM+treatment with H_2S/H_2	82.3±1.7
100 ppm Mo as APTM-1A	82.3±2.9
300 ppm Mo as AHM+treatment with H_2S/H_2	82.2±1.6
300 ppm Mo as AHM	80.3±0.4

CONCLUSIONS

When non-sulfur containing oxomolybdate was used as catalyst precursor for coal liquefaction, complete transformation to active catalyst in situ apparently does not occur under

reaction conditions. Upon recycle, the Mo-catalysts have been observed to be far more active. The inevitable presence of water in the reaction system at the high reaction temperature affects this transformation. If oxothiomolybdate is used as precursor or if oxomolybdate impregnated coal is presulfided prior to reaction, activity for resid conversion improves substantially and is retained for a longer period. In these cases, the catalyst is more active and more resistant to water oxidation. An external sulfur is still necessary with oxothiomolybdate precursors.

ACKNOWLEDGMENTS

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Table 1. Properties of Wyodak Coal and Feed Solvent			
	Coal	Solvent	
	Ultimate Analysis	Heavy Distillate	Deashed Resid
<566°C	-	96.9	14.7
Composition (wt%)			
Carbon	70.62	88.86	89.79
Hydrogen	5.03	9.91	7.26
Nitrogen	1.13	0.44	0.86
Sulfur	0.52	<0.03	0.03
Oxygen (diff)	16.38	0.79	1.33
Ash	6.32		0.73
Ash, SO_3-free	5.46		

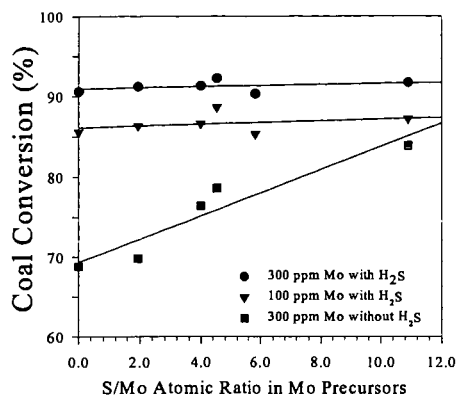| Table 2. Composition of Mo-Based Oxothiomolybdates (wt%)						
	AHM	AOTM	ATTM	APTM-P	APTM-2A	APTM-1A
H	2.59	3.58	3.08	1.30		1.16
N	6.80	11.7	10.77	3.76		3.0
S	0	28.28	49.23	55.05	60.23	72.16
Mo	54.37	43.97	36.92	36.76	31.05	19.91
O (diff)	36.24	12.47	-	3.13		3.77
S/Mo (atomic)	-	1.93	4.00	4.49	5.82	10.87

Figure 1. Effect of S/Mo ratio in precursors on coal conversion in the presence/absence of external H_2S
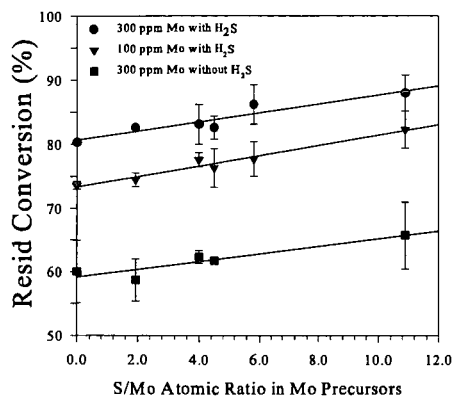

Figure 2 Effect of S/Mo ratio in precursors on resid conversion in the presence/absence of external H_2S.
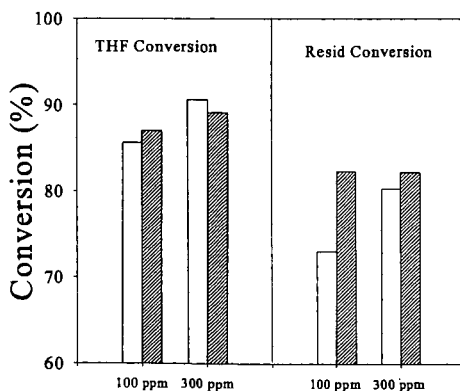

Figure 3. Effect of H_2S/H_2 pretreatment on coal liquefaction with AHM as catalyst precursor. ▭ --- no pretreatment, ▨ --- H_2S/H_2 pretreatment.

ASSESSMENT OF BIMETALLIC AND PARTIALLY-SULFIDED PHOSPHOMOLYBDATES FOR LIQUEFACTION OF WYODAK COAL

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ABSTRACT

Phosphomolybdic acid (PMA) is an excellent catalyst precursor for direct liquefaction of Wyodak coal when well dispersed within the reaction system by impregnating onto the feed coal. Addition of sulfur during the reaction significantly increased the activity of the catalyst. Several partially sulfided phosphomolybdates were prepared and characterized by a variety of analytical techniques. THF and resid conversions with these partially converted precursors were determined when added as particulate material directly to the reaction mixture and when impregnated onto Wyodak coal. The effectiveness of these partially converted intermediates will be related to their physical characteristics and elemental and structural compositions. Nickel and cobalt bimetallic phosphomolybdates were prepared and impregnated on coal. The effect of the co-metal on the activity for solubilizing coal and conversion of coal-derived resid will be compared with other active Mo precursors.

INTRODUCTION

Development of catalysts is important for more efficient coal liquefaction to produce liquid fuels. Dispersed catalyst is understood as the catalytic material employed as particles dispersed on coal or in the reaction media. It provides intimate contact with the surface of coal particles which influence reactions and break the coal structure to gas and liquid products. Many reports have been published on liquefaction using dispersed catalysts, particularly molybdenum and iron sulfide. Molybdenum is often added to liquefaction processes either as the oxide or thiolate water-soluble salts or as molybdenum naphthanate.[1] The active form of molybdenum is not well-known, although it is considered to be molybdenum disulfide. Our studies indicate that intermediate molybdenum oxysulfides may be the active catalyst.[2,3] Lopcz et al. reported that the atomic S/Mo ratio was less than two in the active catalysts isolated from processing heavy petroleum fractions with ammonium molybdate and thiomolybdate.[4]

Most active catalysts are insoluble in common solvents and one method of increasing dispersion is to introduce the catalyst as a soluble precursor.[5-8] Phosphomolybdic acid (PMA) and most bimetallic phosphomolybdates are soluble in water and provide good dispersion.[9] When PMA was impregnated onto coal, THF and resid conversions are comparable to those obtained from various molybdenum salts.[3, 10-12]

The addition of a second metal, such as Ni and Co, can increase hydrogenation and hydrodesulfurization activity. Chiantelli et al. used bimetallic complexes to study the promotional effects of Ni and Co for MoS_2.[13] Garg and Givens reinvestigated the catalytic activity of several impregnated transition metals in coal liquefaction and showed that addition of Ni, Co and Mo salts was effective.[2] Eccless and de Vaux reported that Ni-Mo or Co-Mo gives a very high yield of light oil fractions.[14]

The first objective of this work is to show the performance of sulfided catalysts produced from PMA for coal liquefaction. The second objective is to show the catalytic activities of bimetallic phosphomolybdates for coal liquefaction and to compare them to PMA.

EXPERIMENTAL

Wyodak coal from the Black Thunder Mine in Wright, Wyoming was supplied by Hydrocarbon Technologies, Inc. Proximate and ultimate analysis of the coal are given in Table 1. The recycle solvents were obtained from the Advanced Coal Liquefaction R&D Facilities at Wilsonville, Alabama. Phosphomolybdic acid (PMA) was supplied by Aldrich Chemicals Inc. $Co_3(PMo_{12}O_{40})_2 \cdot xH_2O$ (CoPM), $Ni_3(PMo_{12}O_{40})_2 \cdot xH_2O$ (NiPM) and $K_3PMo_{12}O_{40} \cdot xH_2O$ (KPM) were synthesized in our laboratory.

Sulfidation of PMA was carried out in a 9" x 2" tubular quartz reactor equipped with a furnace, thermocouple and temperature controller. A stream of nitrogen or 8 vol% hydrogen sulfide in hydrogen flowed into the reactor through flowmeters. The exhaust gases from the reactor were passed through a H_2S scrubber filled with NaOH solution and vented to a hood. About one gram of PMA in a porcelain boat was placed into the reactor for sulfidation experiments. After the reactor was purged with nitrogen at ambient temperature to remove air, a stream of 8 vol% H_2S in H_2 was

passed over the sample and the reactor heated to 125, 150, 200, 300 or 450°C. The samples remained at the specified temperature for 4 h at a H_2S-H_2 flow rate of 80 ml/min. In each experiment, a total of 19.2 liters of H_2S-H_2 was passed over the sample. The reactor was subsequently cooled to ambient temperature under nitrogen, and sulfided catalysts (PMA125, PMA150, PMA200, PMA300 and PMA450) were ground to fine powder before use.

Sulfided PMA materials were added to the reaction media in two ways: direct addition of sulfided PMA materials to the reaction mixture and impregnating sulfided PMA materials onto coal. The apparent water solubility of the sulfided PMA materials decreased as the temperature of preparation increased. Coals were prepared by slowly adding in a dropwise manner the water solutions containing the sulfided materials, and any undissolved material, which was normally quite small, was washed onto coal with additional water. Total amount of water used for impregnating the sulfided PMA materials was about 0.5 g per g dry coal. Coals were then dried in a vacuum oven at 96°C and 33 kPa overnight to remove essentially all of the moisture.

The Ni, Co and K salts of PMA were impregnated onto coal from aqueous solutions. The patassium salt was soluble only after adding a few drops of KOH to the water. Coals were impregnated by adding aqueous solutions (0.03 g solution/g dry coal) that contained the appropriate concentration of the individual metal salts to provide a final loading of 300 mg Mo/kg dry coal. During addition, the powdered coal was continually stirred to assure even dispersion. Impregnated coals were used without being dried and contained 11.9 wt% moisture.

Activity tests were carried out in a 50-cc micro autoclave at 440°C and 1350 psig for 30 minutes. The reactor was equipped with a thermocouple, and connected to pressure transducer for monitoring temperature and pressure during the reaction. Experiments were duplicated at least 2 times to confirm the reproducibility. In a typical experiment, 1.75 g of 524°C-distillate (Wilsonville Run 258 period B), 2.8 g of deashed resid (Wilsonville Run 258 period A) and 2.45 g of metals impregnated coal were added to the reactor and pressurized with H_2S/H_2 (3 wt% H_2S in H_2). The reactor was submerged in a fluidized sand bath and agitated continuously at the rate of 400 cycles per minute at the specified temperature. After quenching, solid and liquid products were removed from the reactor using tetrahydrofuran (THF) and the mixture was extracted in a Soxhlet extractor overnight. The THF insoluble fraction was dried in a vacuum oven and weighed. The soluble fraction was distilled under vacuum (modified ASTM D-1160-87) to atmospheric equivalent end point of 524°C to determine the resid and coal conversions.

$$\text{Resid Conv} = \left(1 - \frac{(\text{IOM} + 524°\text{C}^+ \text{Resid (af)})_{\text{Products}}}{(\text{coal (maf)})_{\text{Feed}}}\right) \times 100$$

RESULTS AND DISCUSSION

Molybdenum compounds are widely used in coal liquefaction because of their hydrogenation activity and the case which they can be dispersed in the reaction system or impregnated onto coal. Sulfur or sulfided catalysts are generally added to the reaction mixture to convert them to the sulfided forms under reaction conditions.[15]

PMA was sulfided at elevated temperatures in order to understand the form of the catalyst derived from the precursors.[16] Elemental analysis of presulfided materials are given in Table 2. The activities of these materials were determined by adding these particulate solids to the reaction mixture and by impregnating them from an aqueous solution onto coal. The activity resulting from adding the particulate presulfided materials directly to the reaction mixture was much less than observed by impregnating untreated PMA onto coal (Figure 1). THF conversions decreased as the treatment temperatures increased. They were about 62% for materials treated between 125 and 200°C and decreased to about 57% for materials prepared at 300 and 450 °C. The THF conversion for untreated particulate PMA was 80.7%. Resid conversions (maf) for the sulfided materials varied between 43-48% while untreated particulate PMA gave 42.7%.

Good dispersion of the catalyst on the surface of the coal particles improves conversion by increasing the amount of active surface area in the reaction phase. An approach to achieving catalyst dispersion is to employ a solvent for dispersing the catalyst. Unfortunately, liquefaction catalysts such as pyrhotite, pyrite and molybdenum sulfide are insoluble in all common solvents. Although the soluble precursors may not be catalytically active they transform into active catalysts at elevated temperatures. As an example, the water soluble PMA, which decomposes to intermediate molybdenum oxysulfides at typical liquefaction temperatures, has been used as a precursor to obtain a good dispersion.[7]

Because of the partial solubility of the sulfided PMA materials in water, they were impregnated onto coal from aqueous solutions. The activity of the impregnated coals was higher than observed for the particulate addition of the sulfided materials but not as high as observed for PMA impregnated coal (Figure 2). Both THF and resid conversions were higher for those materials

prepared at the lower temperatures. THF conversion for PMA125 is only slightly less than the PMA impregnated coal, i.e., 89.2 and 92.3%, respectively. Resid conversions varied from 65 to 42% with PMA125 and PMA150 giving essentially the same resid conversion as PMA impregnated coal (64.5%). Higher treatment temperatures resulted in a significant decrease in resid conversions. Although the data indicate that the sulfided materials prepared at lower temperatures are as active as PMA, they do not show any improvement over impregnated untreated PMA.

Activities of metal impregnated coals were compared in Figure 3. Nickel phosphomolybdate (NiPM) and cobalt phosphomolybdate (CoPM) gave almost the same average THF conversions, which was somewhat higher than the average conversion for potassium phosphomolybdate (KPM). The THF conversion for PMA (92.3%) was slightly higher than the Co and Ni salts. The standard deviations for the salts showed significant overlap in the values suggesting no significant difference in these conversions, although the PMA value appears to have statistical significance. The resid conversion of NiPM was higher than the Co and K salts although standard deviations again indicated significant overlap in the values. The NiPM resid conversion is also greater than observed for the PMA impregnated coal (64.5%).

CONCLUSION
Sulfided PMA materials did not show higher catalytic activity than PMA when added directly to the reaction media, and gave lower THF conversion than the non-catalyzed thermal case. The activities of impregnated sulfided PMA materials prepared at 125 and 150°C was comparable to PMA. Conversions decreased for sulfided materials produced at higher temperatures. Apparently, materials prepared at the higher temperatures are not as well dispersed due to their decreasing solubility in water. None of the bimetallic phosphomolybdates (CoPM, NiPM and KPM) improved THF conversion, however resid conversion was higher for NiPM than for the other bimetallic salts or untreated PMA. Resid conversion for CoPM was comparable PMA.

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Table 1. Analysis of Wyodak Black Thunder Coal.

Proximate Analysis	w%	Ultimate Analysis	w%(dry)	Sulfur Analysis	w%
Moisture	8.89	Carbon	70.62	Total	1.94
Ash	5.76	Hydrogen	5.03	Pyritic	0.80
Volatile matter	39.88	Nitrogen	1.13	Sulfate	0.80
Fixed carbon	45.47	Sulfur	0.52	Organic	0.34
		Oxygen (diff)	16.38		
		Ash	6.32		
		Ash, SO_3-free	5.47		

Table 2. Elemental analysis of PMA and the sulfided samples.
S/Mo atomic ratio in feed = 12.3
Sulfidation time = 4 h

	Composition, wt%				Formula
	P	Mo	S	O (diff)[a]	$P_xMo_{12}S_yO_z$
PMA	3.52	49.65	0.00	46.83[b]	$H_{45.6}P_{2.6}Mo_{12}O_{65.8}$ $(H_3PMo_{12}O_{40}\cdot20H_2O)$
PMA125	4.26	59.50	4.95	31.29	$P_{2.7}Mo_{12}S_{3.0}O_{37.8}$
PMA150	4.57	60.97	5.40	29.06	$P_{2.8}Mo_{12}S_{3.2}O_{34.3}$
PMA200	4.74	65.60	4.79	24.87	$P_{2.7}Mo_{12}S_{2.6}O_{27.3}$
PMA300	5.48	66.49	4.93	23.10	$P_{3.1}Mo_{12}S_{2.7}O_{25.0}$
PMA450	5.31	70.11	20.60	3.98	$P_{2.8}Mo_{12}S_{10.6}O_{4.1}$

a. Difference includes oxygen and hydrogen   b. Includes 3 wt% hydrogen
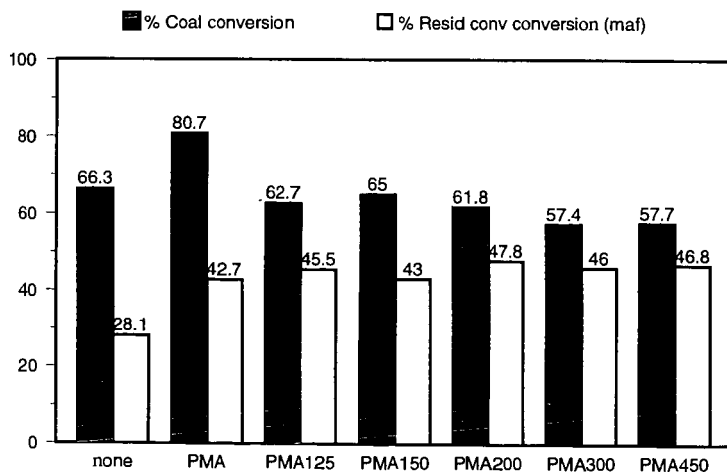
Figure 1. Activity tests from direct addition of PMA and the sulfided PMA materials to reaction mixture.
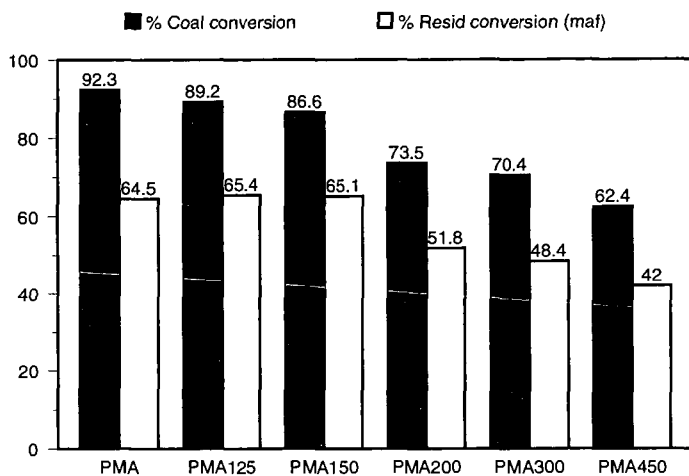
Figure 2. Activities of coal impregnated with PMA and the sulfided PMA materials.
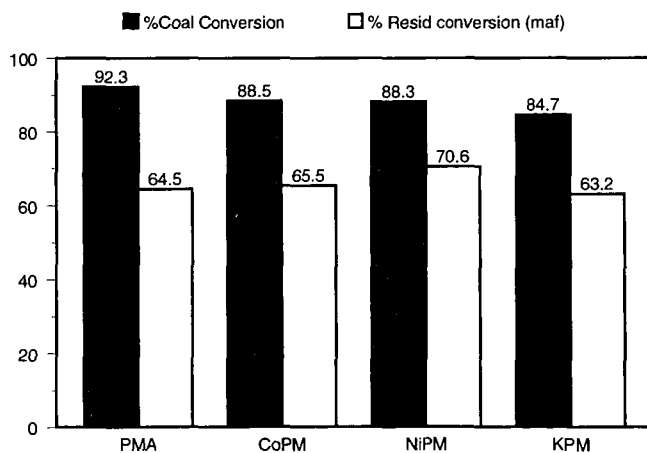
Figure 3. Activities of coal impregnated with PMA, CoPM, NiPM and KPM.

COAL CONVERSION TECHNOLOGIES ON
THE NEW SUNSHINE PROGRAM IN JAPAN

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ABSTRACT
Agency of Industrial Science and Technology (AIST) has been conducting R&D on coal
conversion technologies in Japan.   New Energy and Industrial Technology Development
Organization (NEDO) has been carrying out some R&D projects on coal conversion technologies
as a part of "New Sunshine Program" lead by AIST.   Coal gasification technologies and
liquefaction technologies are major concern for NEDO and the overview of the R&D projects up-
dated is presented in this paper.   In addition, a new project on coal hydrogasification technology
are also outlined.

INTRODUCTION
AIST initiated the **"Sunshine Project"** to develop technologies associated with new
energy in 1974 after the first oil crisis in 1973.   In 1978, the **"Moonlight Project"** for energy
conversion was started followed by the R&D Project on environmental technology in 1989.
These projects were consolidated into the **"New Sunshine Program"** in 1993, aiming to
develop the innovative technologies that could support the sustainable economical growth
while solving energy and environmental issues.   The R&D schedules of coal conversion
technologies in the New Sunshine Program are shown in Table 1 [1, 2].
Both R&D of gasification and liquefaction started under the **"Sunshine Project"** have a
long history (from 1974 for gasification and 1976 for liquefaction).   By now, an integrated
coal gasification combined cycle (IGCC) pilot plant with a capacity of 200 t/d demonstrated
its capability in giving high thermal efficiency and environmental acceptability, while the
operation of an 150 t/d coal liquefaction pilot plant is being carried out.   Basic researches on
coal liquefaction have been constantly conducted at national institutes and universities.   The
R&D of refining coal-derived liquids is still on the stage of laboratory scale.   The project on
coal hydrogasification started in 1996.   This process produces methane directly from coal
and hydrogen with BTX as co-products and is expected to have high efficiency, coal
adaptability, environmental adaptability and cost competitiveness.   The final target is to
commercialize in 2010's [3].

Coal gasification technologies
In 1986, operation of a hybrid gasification pilot plant which employed a pressurized fluidized-
bed gasifier feeding coal and heavy oil mixture was finished.   The project demonstrated
production of high calorific gas containing a high concentration of methane together with high
energy efficiency comparable to other processes.   Following the results of the hybrid gasification,
a coal-based hydrogen production project (HYCOL) started in 1984.   Pulverized coal is gasified
into hydrogen and carbon monoxide in a gasifier under the condition of a pressure of 30atm and a
temperature 1500°C or above.   Gasification is carried out in oxygen-blow one chamber and
two-step spiral flow system.   High purity hydrogen is then produced after processing carbon
monoxide with shift-reaction and other processes.   A pilot plant with a capacity of 20 t/d for

HYCOL was constructed in 1990. The operating research has been completed in 1993.

The history of R&D of IGCC is follows: In 1996, the 200 t/d pilot plant was disassembled after 5 years' operation test, and all data obtained is accumulated to discuss the possibility of construction of a demonstration plant. The organization which lead the R&D was reunified and is now working for the feasibility study of the demonstration plant. The study will continue for two years to conclude whether we should go further or not.

A feasibility study was started on coal hydrogasification technology that employs hydrogen as the gasifying agent and produces high calorific gases with high concentrations of methane in FY1990. A elemental study started in 1996.

Coal liquefaction technologies

There are two streams for R&D of coal liquefaction in Japan. One is the project for brown coal liquefaction which was conducted in Victoria, Australia from 1981 to 1990. The present work is to improve the liquefaction process to make it feasible for a commercial use [4]. The other is on bituminous coal liquefaction of which process is named as "**NEDOL Process**". After 4 years of construction, the pilot plant has started its official operation [5-7]. Some results of the operation will be presented at the ACS meeting. Seven runs of the plant are scheduled over two years and "**Technology Package of the NEDOL Process**" will be documented afterward. "**NEDOL Process**" is also being verified at process supporting unit (PSU) facilities in Kimitsu [8]. It still takes one year or so to start the operation of a 40 b/d PDU, which is now under construction to demonstrate the refining of coal-derived liquids so that it meets the requirements of petroleum market. Meanwhile, basic studies are pursuing the optimization of the hydrotreatment of coal-derived liquids in and the prevention of plugging during refining. We focus on the NEDOL process for coal liquefaction in this presentation.

EXPERIMENTAL

NEDO has been promoting a development of a coal liquefaction technology, since 1980, under "New Sunshine Program" and developed the "NEDOL" process that can attain high light oil yields under relatively mild conditions. The NEDOL process was realized in the 1 t/d PSU based on research and development work through autoclaves, bench scale plants and PDU scale plants. In the PSU, comprehensive experiments have been conducted with several kinds of coals and operating conditions and lots of significant data have been acquired. In parallel with the research and development in the PSU, the 150 t/d pilot plant (PP) was constructed for collecting scale-up data to demonstration and commercial plants. The construction of the PP was finished on July, 1996 and the operation was commenced.

The NEDOL process, shown in Figure 1, consists of four primary units, such as coal preparation unit, coal liquefaction unit, solvent distillation unit and solvent hydrogenation unit. The NEDOL process can attain high oil yield even in relatively low severity condition as shown in Table 2. It has been concluded that ultra fine iron catalyst and hydrogenated solvent bring this high oil yield. In the PSU operation, several kinds of coals have been liquefied and the efficacy of the NEDOL process has been demonstrated. Based on the results of the PSU, a standard coal for the PP operation was determined. Table 3 indicates the analytical data of the standard coal for the PP. The operation of the PP has been conducted in the conditions shown in Table 2 and with the standard coal shown in Table 3 and the results were compared with the results of the PSU conducted in the same conditions and with the same coal.

RESULTS AND DISCUSSION

The results of the PP operation were compared with the results of the PSU operation and the comparison result is indicated in Table 4. Although the results of the PP are not results on 100 % plant load, yields of the PP have a good correlation with the results of the PSU. The yields of the 80 % load in the PP imply that the yields of 100 % load in the PP can attain same yields as the PSU on the same liquefaction conditions. This indicates that scale up data for larger plant will be able to be acquired in comparison of the data between the PSU and PP.

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Table 1. R&D schedule of coal conversion technologies on the New Sunshine Program

R&D items / Fiscal year	Activities (80–00)
Coal liquefaction	
Bituminous coal liquefaction · Direct hydrogenation	design & construction operation (80–82); NEDOL process: design, design & construction, operation (85–00)
· Solvent extraction	design & construction operation
· Solvolysis liquefaction	design & construction operation
NEDOL process	design → design & construction → operation
Brown coal liquefaction	design; design & construction; operation; disassemble study
Coal gasification	
Coal hydrogasification	feasibility study; elemental study
Hybrid gasification	operation
Coal based hydrogen production (HYCOL)	elemental study; design & construction; operation; disassemble study
Low-calorific gasification and power generation (IGCC)	design; design & construction; operation; disassemble study

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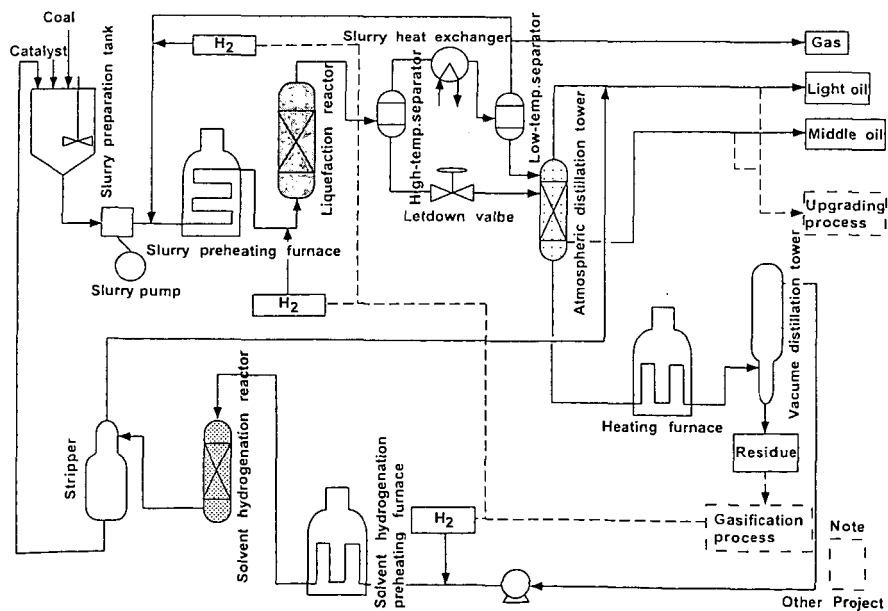
Figure 1.   Diagram of NEDOL Process

Table 2.   Typical liquefaction conditions

	Typical condition
Temperature	430 - 465 °C
Pressure	150 - 190 kg/cm²G
Catalyst	Ultra fine iron sulfide 2 - 3 wt%
Slurry concentration	40 - 50 wt% (dry coal)
Slurry residence time	1 hr
Gas/slurry ratio	500 - 700 Nm³/t
Hydrogen conc. in recycle gas	85 vol %

Table 3.   Typical coal analytical data for the PP operation

Proximate analysis (wt %)		Ultimate analysis (wt % daf)	
Moisture	3.8	C	76.4
Volatile matter	47.4	H	5.8
Fixed carbon	47.7	N	1.8
Ash	4.9	TS	0.3
		O	15.7

Table 4.   Comparison of the yields between the PP and the PSU

	150 t/d PP		1 t/d PSU		
Plant load [%]	60	80	100	100	100
Temperature [°C]	450	450	450	465	465
Pressure [kg/cm²G]	170	170	170	170	190
G/L [Nm³/t]	700	700	700	700	900
Catalyst addition [wt %]	3	3	3	3	4
Residence time [hr]	1.67	1.25	1.0	1.0	1.0
Yields [wt % daf]					
Water	12	11	10.8	11.5	11.4
Gas	18	17	19.7	25.5	26.5
Oil	54	52	51.7	55.5	59.4
Residue	22	26	23.3	14.4	9.9
H₂ consumption	5.9	5.4	5.5	6.9	7.2
Total	105.9	105.4	105.5	106.9	107.2

CONVERSION OF LOW-RANK COALS AND LIGNINS TO PHENOLIC PRODUCTS BY CATALYTIC HYDROGENOLYSIS IN AQUEOUS BASE

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INTRODUCTION

Direct methods of coal conversion to liquids have been studied in depth since the initial experiments were conducted in the late 19th century; however, the identification of methods to lower reaction severity has been slow. Earlier work, as discussed by Schobert,[1] successfully achieved conversion to liquids using very high reaction temperatures and hydrogen pressures (>450 °C and >5000 psi). Reactions at somewhat lower severity (i.e., lower temperature and pressure) were achieved by the use of various catalysts and solvents. These catalyzed reactions can occur at ~ 400-425 °C and hydrogen pressures (initial) of ~900-1000 psi (2500-3000 psi at temperature) in 30-60 minutes. Even under these reaction conditions, economic viability in today's petroleum market still has not been achieved. Researchers continue to seek avenues to further reduce reaction severity.

Some research has shown that for lower rank coals, particularly lignites, reaction severity can be reduced.[2-6] It is thought that the mechanism that drives coal reactions in the 350-450 °C range is the thermolysis of C-C bonds and particularly C-O bonds; lower rank coals contain more oxygen functionality, and therefore, these coals tend to react at the lower end of this temperature region because C-O bonds are weaker than C-C bonds. Derbyshire, et al.[2,3] and Jackson, et al.[7,8] have achieved conversions of ~ 90 % for low rank coals when using various hydrogenation catalysts (Ni/Mo) at lower reaction temperatures of ~ 400 °C and reaction times of 30-60 min. Understanding the complexity of the macromolecular structure and the mechanisms of liquefaction of low-rank coals is important in order to optimize the production of valuable liquid products. The main limitation to lowering the reaction severity of coal liquefaction processes is identifying a reaction method that is not completely dependent on the thermolysis of C-C and C-O bonds for depolymerization.[2-6] Lewis acids (e.g., SnCl$_2$, ZnCl$_2$) do accomplish coal cleavage at slightly lower temperatures (~ 350 °C and 1 h reaction time).[9-14] Unfortunately, large quantities of catalyst must be used and the chlorides in these compounds cause significant reactor corrosion.[9-14]

The present primary energy project at UTPB relates to the reductive depolymerization of biomass polysaccharides to C$_5$ and C$_6$ hydrocarbons.[15] Since coal essentially represents a degraded biomass, it is envisioned that the reactions used to fractionate biomass into polyols and lignins, and to further react the latter, might be equally successful when applied to low rank coals. The reaction conditions initially employed were based on Russian reports of sequential catalytic hydrogenolyses in acid and base. This was done to first convert carbohydrates to C$_5$ and C$_6$ polyols at 185 °C and 700 psi (initial) and then lignin into phenolic materials at 280-320 °C and 700-900 psi hydrogen (initial), respectively.[16] Because of the very high conversions of raw biomass by the "biomass-to-polyol" process and because of some similarities in the structures of lignin and lignites, we expected similar sequential reactions could have a significant effect on the conversion of low rank coals to liquids. We chose to focus on the base hydrogenolysis omitting a prior acid hydrogenolysis, as this step had the greatest effect on the lignin in biomass.[16] This paper focuses on reacting DECS-1 coal and lignin at 240, 270, and 300 °C, 700 psi (initial) for 6 h in NaOH solution and subsequent characterization of the products by solution NMR and pyrolysis-GC/MS.

EXPERIMENTAL

The coal was obtained from the Pennsylvania State University Coal Sample Bank (COPL), denoted by DECS-1. The coal rank of DECS-1 as determined by the COPL is subbituminous C. Elemental analysis for the coal and the solids (acids) from the NaOH-solubles was done by Galbraith. For the coal, the elemental analysis was carbon % (C) - 58.7 , hydrogen % (H) - 4.7 , nitrogen % (N) - 1.0, sulfur % (S) - 1.2, and oxygen % (O) (by difference) - 18.1. The ash content is 16.3 %. The lignin used is a commercial hydrolytic lignin obtained from Aldrich Chemical Company.

Reactions of coal with NaOH were carried out in a 1-gallon Parr stirred autoclave. The reactions were run at 240, 270, and ~300 °C under 700 psi hydrogen (initial) atmosphere using a carbon-supported ruthenium catalyst (Ru/C) purchased from Aldrich (5 % Ru). About 20 g of coal or lignin was loaded with 2 g of catalyst (Ru/C) and 2 L of 1.5 % (wt) NaOH. Reactions were run at the designated temperature for ~6 h although initial heating and final cooling of the reactor could take

several hours depending on the final temperature. The contents of the reactor were filtered and the solid washed with water to remove all of the base (until pH ~7).

Figures 1 and 2 are schematics of the procedure used to extract all of the soluble organic products resulting from the reaction. Neutral oils were obtained by washing the initial solids and aqueous layer (including rinse water) with methylene chloride CH_2Cl_2 (see Figure 1). The NaOH-solubles were acidified with concentrated H_2SO_4 to pH ~2 and heated to ~ 80°C to promote coagulation and filterability; the precipitated solids (acids) were then filtered (see Figure 2). All the solids from the initial filtration procedure and the acidic solids were extracted (using sonication) with CH_2Cl_2 followed by extraction (using sonication) with tetrahydrofuran (THF). The percent conversion was determined from the difference between the initial weight of the dry coal and catalyst and the final dry weight of solid residue and catalyst, per initial amounts.

All organic products were analyzed by ^1H and ^{13}C solution NMR. Samples were dissolved/filtered in chloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO-d_6) and spectra obtained by a Bruker 250 MHz Avance DPX NMR.

Pyrolysis-GC/MS was performed with a Hewlett Packard (HP) 18580A pyroprobe interfaced to a (HP 5890/5970) GC/MS. Chromatography was carried out on a 25 m x 0.22 mm i.d. x 1.0 μm film thickness column coated with a BPX5 phase (modified to 5% phenyl siloxane). The GC oven temperature was programmed to increase from 40°C, initially held for 2 min., at a rate of 4° C/min to 300 °C (maintained for a further 30 min). The samples pyrolyzed were the DECS-1 raw coal and the solids (acids). On pyrolysis at 850 °C about 55-60 % of both samples was vaporized.

RESULTS AND DISCUSSION

Percent of Coal Extracted

Figure 1 is a schematic of the initial treatment of reactor contents, whilst Table 1 shows the total conversion and the material balance information. For all reactions, > 90% of the organic matter from DECS-1 was extracted and/or dissolved. About 85-95 % of the coal was extracted into the aqueous base solution. As the temperature increases, then the amount of coal extracted into the aqueous base slightly decreases. For reactions at 240 and 270 °C, the other materials extracted from the remaining catalyst/organic/ash residue (CH_2Cl_2- and THF-soluble compounds) amounted to about 4-5 %. However, at 300 °C, the CH_2Cl_2- and THF-soluble compounds increase to 15 %. This suggests the reaction chemistry is indeed changing with increasing temperature and this may account for the higher proportion of neutral compounds and less of the acidic compounds at higher temperature, i.e., more thermolytic reduction (see Table 1).

Figure 2 is a schematic of the product work-up of the NaOH-solubles. Table 2 shows a breakdown of the product into fractions. The NaOH-solubles were acidified with H_2SO_4 to a pH of ~2. The solution then formed a dark brown precipitate that was briefly digested (to coagulate solids) at 80 °C before filtering. The remaining filtrate was a clear, pale yellow solution with a·strong phenolic odor. The 240 °C reaction had the highest percent NaOH-solubles, 95 %, with 49.7% solids and 45.8 % (determined by difference) of material either left in solution or gaseous reaction products. At 270 °C, a lower amount of coal was solubilized by the base, 87.5 %, but a much greater proportion, 72.7 %, were solids. At 300 °C, only 84.5 % of the coal was solubilized by the base, but only 34.9 % precipitated out. Since the majority of the coal was extracted into the base solution, determining the product character of this fraction is important in understanding the reaction chemistry. However, elucidation of the composition of both the solid and water-soluble materials has proved to be complicated and is to-date not complete. Clearly, phenols (A2 acids) and carboxylic acids (A1 acids) would be expected to be dissolved into aqueous base but polyfunctional compounds remain in the water layer even after neutralization. The variability in the ratio of precipitated acids versus water-soluble compounds is also being addressed. Results from the present methods of analysis are outlined below.

NaOH-soluble Products

Most of the work completed has been done on the 240 °C reaction solids from the acidification of the base solution. The elemental analysis of the NaOH-soluble solids from the 240 °C reaction is 64.7 % C, 5.4 % H, 1.4 % N, 1.2 % S, 1.1 % ash, and 26.2 % O (by difference). The H/C ratio is 1.0 and the O/C ratio is 0.3, compared to the coal H/C, 0.98 and the O/C, 0.23. The H/C of the product is essentially the same as the coal whilst the O/C ratio is significantly higher than that of the coal, suggesting at 240 °C hydrolysis mostly accounts for the strong oxygen increase and not much hydrogenation has occurred. In fact, more hydrogen is consumed at higher temperature.

None of the solids (acids) proved soluble in CH_2Cl_2 or other less polar solvents. The material is therefore thought to be very polar and possibly also of very high molecular weight, albeit a reduction of the large macromolecules in the coal to smaller oligomers is anticipated. Solution GC/MS analysis revealed little molecular information from the solid NaOH-soluble product. This material did prove soluble to varying degrees in THF, DMSO, and pyridine. Solution ^1H NMR was obtained using the

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polar solvent DMSO-d_6. The ^{1}H NMR is shown in Figure 3 (a). The main feature of the proton NMR is the noticeable -OH or -CH-O- functionality. Unfortunately, the concentration of this solution was not high enough for ^{13}C NMR detection.

Figure 3 (b) and (c) shows the pyrolysis-GC/MS of DECS-1 coal and of the solid product from the NaOH-solubles. Significantly fewer aliphatic and large aromatic compounds are detected from the NaOH- solubles than from the parent coal. These compounds may be present in a different fraction obtained by extraction with other solvents. The compounds in the pyrolysis-GC/MS of the NaOH-soluble product have been identified as predominantly alkylated aromatic compounds with or without -OH functionality. Work will be continued to more accurately determine the structure and/or molecular weight of the NaOH-soluble solid products and will likely include direct MS of the solids with chemical ionization and gel chromatography for polymer size distributions.

The liquids that remain in the water have not yet been completely isolated. Following exhaustive extraction with CH_2Cl_2, some color and odor remained in the water indicating that not all of the organic was extracted. Work continues to more efficiently extract the compounds from the water so as to complete the material balance. Once released these products will also be analyzed by GC/MS. Organic acids and alcohols will first be derivatized to less polar and more volatile esters. Several derivative methods are being screened, e.g., acetylation according to Thring et al.[17]

Comparative Reactions

As stated earlier, these reactions of coal were suggested as an extension of lignin reactions in the literature, so a comparative reaction with lignin was done under these conditions. In our case, however, as noted in Tables 1 and 2, less lignin reacted than the coal reaction at 240 °C. Lignin reactions are higher temperatures are also planned.

The amount of coal extracted under these reaction conditions is remarkable as most reactions at these temperatures produce little if any product. For example, Garcia and Schobert[18] showed with coals of high organic sulfur content that about 8.8 % THF-soluble material could be extracted at 250 °C. This increases up to ~50 % at 325-350 °C when using a molybdenum catalyst in a hydrogen atmosphere (the reactor used in this case was a "tubing bomb" type and caution in comparing this to a stirred autoclave must be noted). Most coal liquefaction reactions produce high conversions at 400-450 °C, and most of the product is composed of lighter molecular weight materials than produced in the reactions reported here. One research group, Hulston et al.,[7,8] used NaOH or NaAlO$_2$ combined with a hydrogenation catalyst (Ni/Mo) at 365 °C to produce significantly higher conversions to CH_2Cl_2-soluble products than when using the Ni/Mo catalyst alone, but the increase in conversion is noted with low-rank coals only. It is also expected for our reaction conditions that coals of rank higher than subbituminous will not convert as easily because of the significantly lower oxygen content of bituminous and anthracite coals. While the ultimate goal of high conversion efficiency of coal into small phenolic liquids has not yet been achieved, a significant amount of liquefaction and a remarkably high conversion to more soluble/extractable products (with little mineral matter left in the organic material) has been realized. Further analytical data are required to show the extent of conversion to small (liquid) molecules.

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Table 1: Conversion information for reactions of DECS-1 and lignin.

Temp °C[a]	Feed	Reactor Load (g)	% NaOH-solubles[b]	% Other[c]	Total	Psi
240	DECS-1	20	95.5	4.7	100	700
270	DECS-1	20	87.5	5.7	93.4	700
306	DECS-1	20	84.2	15.8	100	500
240	Lignin	20	78.9	9.0	87.9	700

a All reactions were 6 h at temperature shown; does not include ramp times.
b Includes any gas that may have been generated because this is determined by difference.
c Methylene chloride-solubles + tetrahydrofuran-solubles.

Table 2: Yield information for the NaOH-soluble portion of the coal. This fraction was acidified with H_2SO_4 to a pH of about 2 and solids filtered out (see Figure 2 for flow diagram).

Temp °C[a]	Feed	% NaOH-solubles[b]	% Solids	% H_2O-solubles[c]	Total
240	DECS-1	95.5	49.7	45.8	100
270	DECS-1	87.5	72.7	14.8	93.4
306	DECS-1	84.2	34.9	49.3	100
240	Lignin	78.9	31.5	47.4	87.9

a All reactions were 6 h at temperature shown; does not include ramp times.
b Includes any gas that may have been generated because this is determined by difference.
c H_2O-solubles are the compounds that remain in solution but also includes any gas that may have been generated.
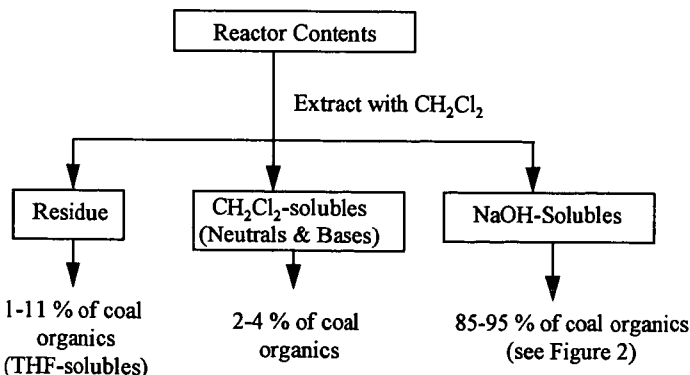
Figure 1: Initial product work-up of coal from reactor. The residue also contains ash and recovered Ru/C catalyst.
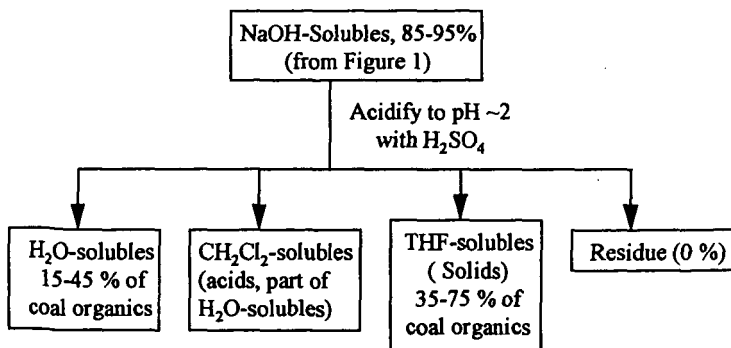
Figure 2: Schematic of product work-up of the aqueous NaOH fraction, the major portion of the coal.
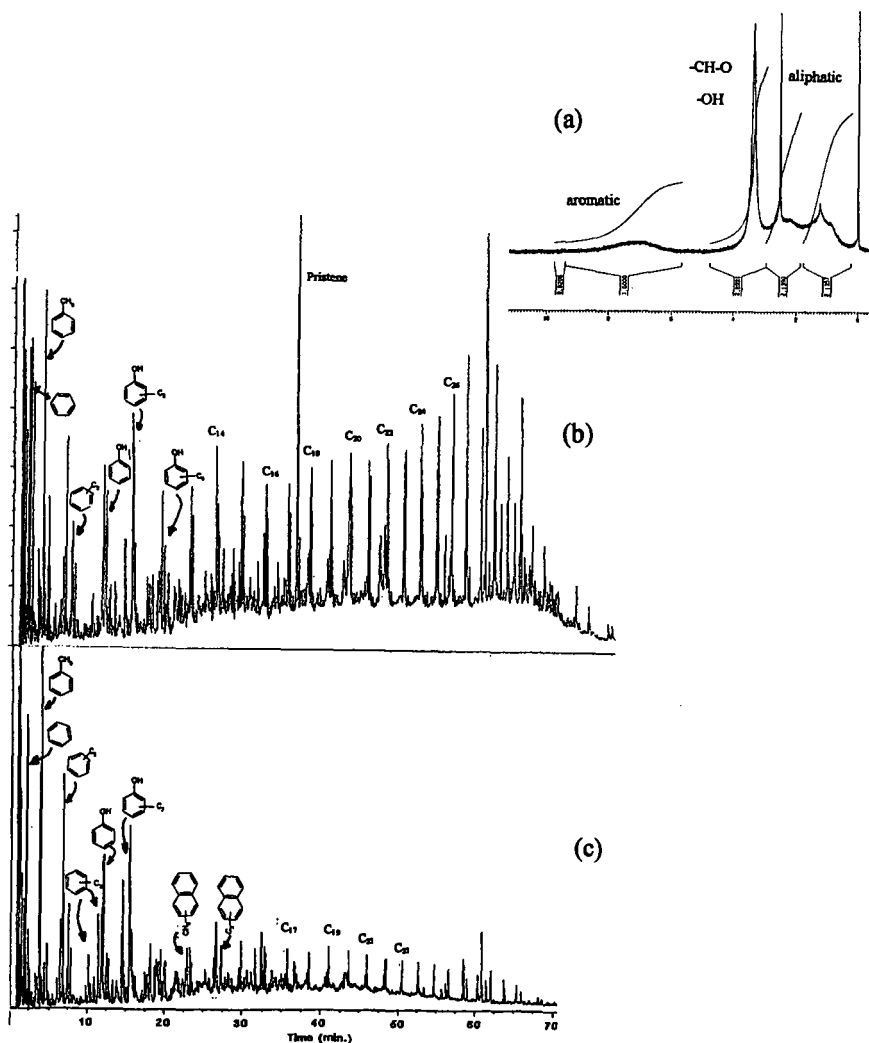
Figure 3: Spectra for: (a) ^{1}H NMR of NaOH-soluble solids (acids), (b) pyrolysis-GC/MS of DECS-1, and (c) pyrolysis-GC/MS of NaOH-soluble solids (acids).

EFFECT OF OXYGEN COMPOUNDS ADDITION ON THE HYDROCRACKING OF ALKYLPHENOLS

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ABSTRACT

To produce and purify useful compounds in tar from coking and from low temperature pyrolysis of coal, hydrocracking of alkylphenol mixture is very important reaction. In this study, the effect of oxygen compounds such as dimethylcarbonate(DMC) addition on the hydrocracking of alkylphenols was investigated to decrease hydrogen loss by the production of water. Hydrocracking of three dimethylphenols(DMP) was carried out using atmospheric flow apparatus with quarts reactor at 700°C, residence time of 3-10 sec and hydrogen to reactant mole ratio of about 10. From the hydrocracking of 3,5-DMP without DMC, m-xylene and m-cresol were produced with the production ratio of 1:1.8. However the dehydroxylation to produce m-xylene was decreased by the addition of 10% DMC with the production ratio of 1:2.7. Similar reaction behavior was observed in the hydrocracking of 2,5-DMP. These are considered due to the strong interaction between DMC and hydroxyl group. Relationship between reaction behavior and molecular structure would be also discussed.

INTRODUCTION

Mild gasification and low temperature pyrolysis are considered to be the most promising process for high-moisture, subbituminous and lignite coal to produce upgraded solid fuel with high heating value and low sulfur, and to produce a useful liquid fuel. However these liquid products contain considerable amounts of oxygen, and are rich in alkylphenols with alkylbenzenes and alkyl-naphthalenes.[1] Gas phase thermal demethylation of a series of methyl substituted benzenes under a excess hydrogen stream has been a subject of many investigators. Reaction behavior, including kinetics, and product distribution for toluene and methylbenzenes can be accounted for by the following free radical mechanism. [2]
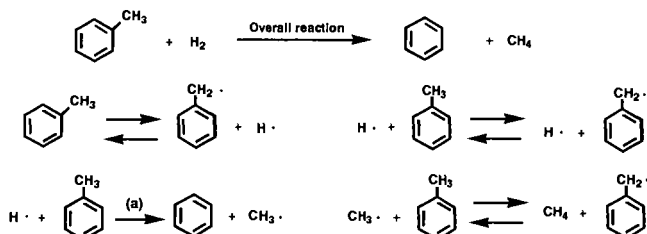
In the above chain scheme, the propagation rate is effectively controlled by reaction (a). This reaction can be pictured as a perpendicular approach to hydrogen atom to phenyl carbon atom, to which methyl group is attached. We have found the same mechanism can be applied for the demethylation of methylnaphthalenes, and the relative reactivities of both methylbenzenes and methyl-naphthalenes have been correlated with the reactivity indices, theoretically calculated by molecular orbital method. [3,4] According to the results for methyl substituted aromatic compounds and the reaction behavior for the other alkyl aromatic compounds, demethylation rates for methylnapthalenes are generally higher than that for methylbenzenes, and the removal of higher alkylgroup takes place competitively with demethylation. In this reaction, aromatic structure does not cracked, and simple aromatic compounds, without having alkyl substituents, are produced with high selectively in the presence of excess hydrogen.

On the other hand, kinetic studies of the thermal hydrocracking of cresols, and 2,4,6-trimethylphenol have been discussed in terms of the reaction mechanism by Davies et al [5], Kawase et al [6], and Moghul et al [7]. The same type of kinetic equation with dimethylation, and the following concurrent reaction scheme have been proposed to account for the experimental measurement of the reaction rate, and the product distribution.
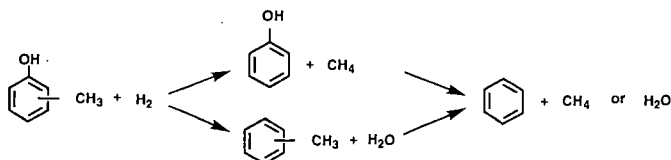
However the relationship between molecular structure and kinetic observations has not yet been explained satisfactory. In this reaction, hydrogen was consumed to produce water by dehydroxylation.

In this study, the effect of oxygen compounds addition on the hydrocracking of alkylphenols was investigated to decrease hydrogen consumption due to the production of water.

EXPERIMENTAL

Commercial reagent grade dimethylphenols(DMP), dimethylcarbonate(DMC) and diethylcarbonate(DEC) were used as received. Thermal hydrocracking of DMP was carried out using a small atmospheric flow apparatus at temperatures of 700°C with residence times of 3-10 sec, and hydrogen-to-reactant molar ratio of more than 10. The reactor was made of a quartz tubing, 21.5 mm in inside diameter and 120 mm in length, and was equipped with a thermo-sheath placed along its central axis. Annular space of the vessel was filled with 10-20 mesh quartz tips, resulting in a free volume of about 18.3 ml. DMP were introduced into the reactor quantitatively by using a small liquid feeding pump, and hydrogen stream was supplied by using a mass flow controller. DMP was mixed with an adequate amount of toluene as a standard reference and 10% DMC or DEC in some of the experimental runs. Gaseous and liquid products were subjected to a conventional gas chromatographic analysis.

RESULTS AND DISCUSSIONS
Reaction behavior of DMP

From the hydrocracking of 3.5-DMP mixed with toluene, benzene from toluene, m-xylene and m-cresol with trace of phenol from DMP were mainly produced with methane. The conversion of toluene and 3,5-DMP with and without DMC were illustrated in Fig.1. These show good fittings of first-order kinetic equation with respect to both toluene and 3,5-DMP. Similar reaction behavior was also observed for 2,5- and 2,6-DMP, however, the conversion ratio of DMP to toluene calculated by first-order rate low was same in all three cases with and without DMC. Products distribution at 700°C from 3,5-DMP are shown in Fig.2 and Table 1. 63.5 mol % m-cresol and 34.5 mol % m-xylene were produced with production ratio of 1.8 from the hydrocracking of 3,5-DMP at 700°C with residence time of 5sec without DMC. This result indicates the rate of demethylation is faster than that of dehydroxylation. From the overall relative first-order cracking rate and the product distribution, the rate per one equivalent methyl and hydroxyl groups for three DMP's were calculated as shown in Fig. 3. The specific rates of demethylation and dehydroxylation are affected by both number and position of substituents of the reactant molecule. Removal of the substituent at ortho position of DMP is quite definitely easier than that of toluene.

Effect of DMC addition on the hydrocracking of DMP

From the hydrocracking of 3,5- DMP mixed with toluene and DMC, observed conversion for both toluene and 3,5-DMP with 10% DMC was higher than that without DMC as shown in Fig.1. The production of m-cresol increased and that of m-xylene decreased by the addition of 10% DMC as shown in Fig.2 and Table 1. The production ratio of m-cresol to m-xylene changed drastically from 1.8 to 2.7 by the addition of DMC. This indicates the dehydroxylation, caused by the attacking hydrogen atom to the phenyl carbon adjacent to hydroxyl group, was prevented by the strong interaction between DMC and

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hydroxyl group in 3,5-DMP. Similar effect was observed by the addition of DEC. Contrary to these, demethylation was accelerated probably by the indirect electronic effect of DMC. However, in the case of 2,5-DMP, the effect of DMC addition on the products distribution was not strong, and the production ratio of cresols to p-xylene changed only from 3.0 to 3.6, as shown in Table 1. The decrease of p-xylene and the increase of cresols in the products distribution was less than 12 mol%. It was thought that the interaction between DMC and hydroxyl group in 2,5-DMP was slightly hindered by the neighboring methyl group at ortho position. Therefore the effect of DMC on the dehydroxylation was weakened by the steric hindrance.

On the other hand, there were no differences in the product distribution and the conversion from the hydrocracking of 2,6-DMP, as shown in Table 1. It was very clear that the interaction between DMC and hydroxyl group was almost completely disappeared by the neighboring two methyl groups at ortho position.

CONCLUSION

The strong effect of DMC addition on the products distribution was observed from the hydrocracking of 3,5-DMP at 700°C. The production ratio of m-cresol to m-xylene changed drastically from 1.8 to 2.7 by the addition of DMC. These are considered due to the strong interaction between DMC and hydroxyl group in 3,5-DMP. Similar reaction behavior was observed for the case of 2,5-DMP, however, the production ratio of cresols to p-xylene increased only 20% from 3.0 to 3.6. Moreover, there were no differences in the products distribution and the conversion for the case of 2,6-DMP. These indicate that the interaction between DMC and hydroxyl group in 2,5- and 2,6-DMP is slightly and strongly hindered by the neighboring methyl group in the molecule. These findings suggest that the addition of DMC can decrease hydrogen consumption on the hydrocracking of alkylphenols. These are also very valid to concentrate and purify phenol and cresols economically by the hydrocracking of coal derived tar.

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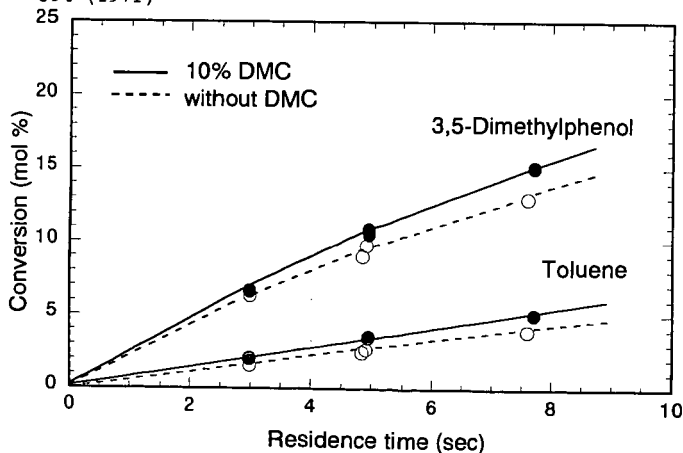
Fig. 1 Hydrocracking of 3,5-Dimethylphenol at 700°C
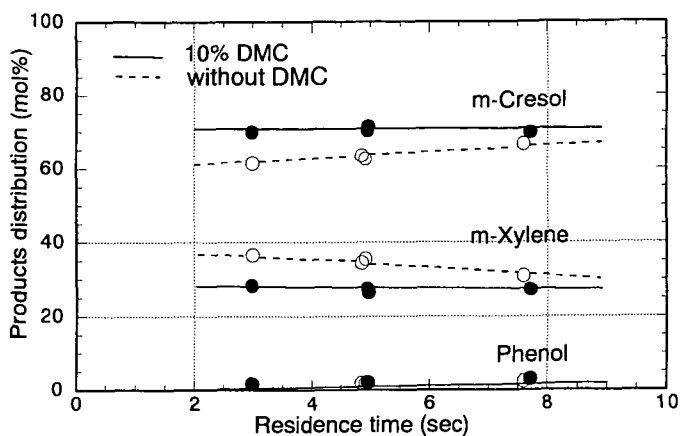
Fig. 2 Products Distribution from the Hydrocracking of 3,5-Dimethylphenol at 700°C

C (1.0)	OH (1.3)	OH (1.6) C (3.6) C (1.3)	OH (2.1) C C (5.0)
1.0	3.7	6.8	7.5
Toluene	3,5-DMP	2,5-DMP	2,6-DMP
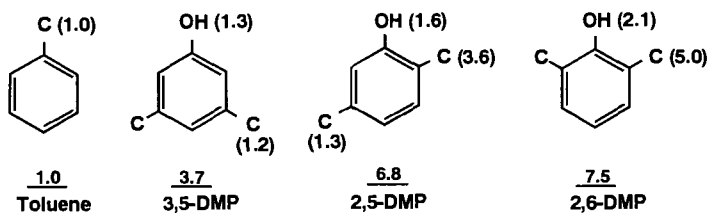
Fig. 3 Relative Rates of Demethylation and Dehydroxylation at 700°C

Table 1   Products Dstribution at 700°C, 5sec.

	3,5-DMP			2,5-DMP		2,6-DMP	
Additive	non	DMC	DEC	non	DMC	non	DMC
Conversion (mol%)							
DMP	9.0	10.5	8.8	20.3	20.9	23.3	23.9
Toluene	2.5	3.5	2.9	3.3	4.0	3.5	3.9
Product distribution (mol%)							
m-Xylene	34.5	26.5	26.4			28.0	28.0
p-Xylene				24.2	21.2		
Phenol	2.0	2.1	1.6	2.7	3.0	4.7	4.9
o-Cresol				19.7	20.8	67.3	67.1
m-Cresol	63.5	71.4	72.0	53.4	55.0		
Cresols/Xylene	1.8	2.7	2.7	3.0	3.6	2.4	2.4

COPROCESSING REACTIONS OF ILLINOIS #6 COAL WITH HONDO PETROLEUM RESID

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KEY WORDS: Petroleum Resid, Coprocessing, Illinois # 6 Coal, and Hondo Resid

INTRODUCTION

Petroleum crude is becoming heavier and the amount of vacuum tower resids produced in refining has been steadily increasing. Many have suggested that the combination of coal liquefaction and heavy resid upgrading has economic and processing advantages over the direct liquefaction of coal.[1-12] Because petroleum resids are still hydrogen rich materials (H/C ≈ 1.5) when compared to coal (H/C ≈ 0.8), the amount of hydrogen required in a combined process should, in principle, be less than that required to produce the same quality products from a stand-alone coal liquefaction facility. It is generally believed that the petroleum resid in coprocessing serves as hydrogen transfer agents for coal conversion; in essence the resid replaces the donor solvent in direct coliquefaction. On the other hand, coprocessing can also improve the quality of the petroleum resid used by the removal of the vanadium and nickel complexes since the undissolved coal could act as a trap for the metal removed from the resid.[13] Thus, coprocessing is beneficial in reducing the deposition of coke and trace metals on a hydroliquefaction catalyst.[2-3, 14-15] The liquids produced by combined processing may also be more amenable to downstream processing and further refining via existing technology and equipment, than liquids from a purely coal fed plant would be. It seemed appropriate to investigate the reaction pathways and explore the conditions for the maximum conversion of both coal and resid to a liquid fuel precursor.

Vanadium and nickel, the principal metals in petroleum resid, are present in structures such as porphyrins and the more condensed asphaltenes in concentrations ranging up to 1300 ppm by weight.[16] During catalytic hydroprocessing for sulfur and nitrogen removal, these metal-bearing molecules undergo hydrodemetallation (HDM) reactions leading to metal deposition and catalyst poisoning. The removal of vanadium and nickel has been investigated widely for this purpose. However, most researchers only selected model compounds of vanadium and nickel porphyrins as subjects for study because of the complication of real petroleum resid systems.[2-3, 16-21]

The objectives of the present study are: (1) to identify conditions for maximum removal of metals, mainly Ni and V, present in petroleum resid using coal with the resultant product becoming a feed to catalytic desulfurization and cracking that does not severely shorten catalyst life; (2) to optimize conditions for the conversion of both coal and resid to a liquid fuel precursor. The catalytic coprocessing of Illinois #6 coal with Hondo resid (850 °F⁺ or whole resid) was carried out using $(NH_4)_2MoS_4$ as catalyst at different temperatures and at 1000 psig of H_2 (cold). The influence of reaction time, and the ratio of resid to coal on the reactivity and product distribution from coprocessing were investigated. The effect on the coprocessing of hydrogenating Hondo resid in a pretreatment step was also studied. The effects of catalysts on coprocessing were studied using $(NH_4)_2MoS_4$, presulfidized $CoMo/Al_2O_3$, $Mo/Fe_2O_3/SO_4^{2-}$ and no catalyst. Ni and V removal was quantified by ICP measurements.

EXPERIMENTAL

The Hondo resid (whole resid: Anal. %C, 83.87; %H, 10.19; %N, 1.01; %S, 4.07; Ni, 78 ppm; V, 150 ppm and hexane insolubles, 25.6% or 850 °F⁺ resid: Anal. %C, 83.60; %H, 10.11; %N, 1.00; %S, 4.23; Ni, 150 ppm; V, 290 ppm and hexane insolubles, 29.5%) obtained from the Federal Energy Technology Center at Pittsburgh and was stored under ambient conditions. The resid is semisolid at room temperature so that it was necessary to heat it to about 100 °C to make it fluid enough to pour into the reactor. Illinois #6 coal was selected for the coprocessing because it has the best demetallation effect.[13] Illinois #6 coal (~60 mesh) was obtained from the Pennsylvania State Coal Sample Bank. The hydrogenation catalyst NiMo/Al₂O₃ (Katalco, 6.7% NiO% and 27.0% MoO₃) was presulfided at 350 °C for two hours. The hydrogenation experiments were completed using 27 cm³

tubing reactors at 1500 psig of H_2 (cold) for 1 h at 350 °C. Coprocessing experiments were carried out in the same tubing reactors as for the hydrogenation. Reactants were brought to the set-point temperature, usually within 10 min, by immersing the reactor in a preheated, fluidized sand bath. The reactor was shaken horizontally (3 times/s) to ensure adequate mixing. At the end of a 1 h reaction time, the reactor was removed from the sand bath and allowed to cool at room temperature for 5 mins, and was then quenched in cold water. Reaction products and solids were removed and extracted with THF, and then the solvent was removed with a rotary evaporator. The THF soluble portion was dried under vacuum for two hours and weighed. The THF insoluble residue remaining in the Soxhlet extractor thimble was also dried for two hours under vacuum. Next the dried THF solubles were extracted with cyclohexane. The cyclohexane was removed from the oil sample using a rotary evaporator. The cyclohexane insoluble residue is referred to as asphaltenes. The cyclohexane soluble portion is referred to as oil. $(NH_4)_2MoS_4$ (Aldrich) was used as received to impregnate the coal from aqueous solution by the incipient wetness technique. The coprocessing catalyst was added to the coal before coprocessing based on 300 ppm of Mo. The ICP analyses were completed by DataChem Laboratories and American West Analytical Laboratories, Salt Lake City, UT. Elemental analyses were completed by Atlantic Microlabs, Norcross, Georgia. Total conversion of coal, asphltenes conversion and conversions to product fractions were defined on an ash-free basis as follows :

total coal conversion: $Y_T = 100(1-Y)$; $Y = (W_I - W_C - W_{ash})/W_{maf}$

asphaltenes conversion (from coal and resid): $Y_{AC} = 100[1- (W_A + W_{ash})/(W_{maf} + W_{RA})]$

coal conversion to asphaltenes: $Y_{CCA} = 100[W_A - W_{RA}(1-Y_{AC})]/W_{maf}$

coal conversion to oils and gases: $Y_{O+G} = 100(Y_T - Y_{CCA})$

where W_I, W_C, W_{ash}, W_A, W_{maf} and W_{RA} are masses of THF insoluble products, catalyst, ash, asphaltenes (cyclohexane insolubles), moisture- and ash-free coal and asphltenes from resid respectively; Y_T, Y_{AC}, Y_{CCA} and Y_{O+G} denote the yields of total conversion, asphaltenes conversion (from coal and resid), coal conversion to asphaltenes and coal conversion to gas + oil, respectively.

RESULTS AND DISCUSSION

Effect of Hydrogenation of Petroleum Resid on the Coprocessing. Table 1 shows the effects of a hydrogenation pretreatment of the Hondo resid (whole or 850 °F⁺) on the catalytic coprocessing of Hondo resid with Illinois #6 coal. After hydrogenation pretreatment of Hondo resid (whole or 850 °F⁺) using presulfidized NiMo/Al$_2$O$_3$, the coal conversions from the coprocessing were increased from 84.3% and 82.9% to 96.6% and 91.4%, respectively for whole and 850 °F⁺ resids. These results clearly demonstrate that the hydrogenated Hondo resid (whole or 850 °F⁺) is a better coprocessing solvent than unhydrogenated Hondo resid. The difference is probably attributable to the formation of hydropolyaromatics in the hydrogenated Hondo resid. This trend has been observed by other investigators[2,8] and our previous work on the coprocessing of coal and hydrogenated vacuum pyrolyzed tire oil.[22] The difference of the coal conversion between the whole and 850 °F⁺ resid is very small because the 850 °F⁺ resid represents 91% of the whole resid. It seems that the asphaltenes conversion from both resid and coal to gas and oil is independent of the hydrogenation pretreatment.

The ICP analyses for Ni and V of the coprocessing products from Illinois #6 with Hondo resid and hydrogenated Hondo resid are summarized in Table 2. After coprocessing, the Ni and V in oil (cyclohexane solubles) were not detected above the limit of detection for the coprocessing of whole resid or hydrogenated whole resid with the coal. Most of the Ni and V was trapped in the ash/char. There was more Ni than V in asphaltenes even though the concentration of V was larger than Ni in the original resid samples.

Effect of the Coprocessing Reaction Time. Table 3 shows the results of the coprocessing of Hondo resid (850 °F⁺) with Illinois #6 coal at different reaction times. The asphaltenes conversion from both resid and coal to gas and oil was increased from 46.1% at 10 min to 71.7% at 80 min. Parallel with the asphaltenes conversion, the asphaltenes for maf coal was decreased from 29.0% at 10 min to 8.75% at 8.7 min, and the gas and oil increased from 49.7% at 10 min to 77.0% at 80 min. In contrast, the total coal conversion did not change much with increasing reaction time. The ICP analyses of Ni and V shown in Table 5 indicate that for most cases the Ni and V in oil were below the detection limits and most of the Ni and V were trapped in the ash/char. It seems that Ni in asphaltenes and in ash/char is independent of reaction time; however, V in asphaltenes decreases with increasing reaction time and V in ash/char increases with increasing reaction time. Hung and Wei observed the same phenomenon when they investigated the hydrodemetallation kinetics of vanadyl

etioporphyrin (VO-Etio) and Nickel etioporphyrin (Ni-Etio).[17]

Dependence on Resid/Coal. The results of changing the resid/coal ratio on the coprocessing of Hondo resid (850 °F$^+$) and Illinois #6 coal are given in Table 4. When the amount of coal was fixed at 1 g, the asphaltenes conversion from both resid and coal to gas and oil was decreased from 64.9% at 1 g of resid to 55.4% at 3 g of resid. Correspondingly, the total coal conversion was decreased from 93.0% to 70.5%, asphaltenes from maf coal increased from 4.9% to 25.2%, and the gas and oil decreased from 88.1% to 45.3%. These trends are related to the limited hydrogen gas available since we used the same amount of hydrogen gas at 1000 psig (cold). When the resid was raised to 5 g, the total coal conversion dropped to only 6%, the asphaltenes conversion came mainly from the resid and was increased to 71.7%. When coal/resid was 0.2 g/1.8 g, no coal conversion was observed and a 60.4% asphaltenes conversion was totally dominated by the resid. When the ratio of coal to resid was adjusted to 1.6 g/0.4 g and 1.8 g/0.2 g, the total coal conversions were 23.1% and 20.1%, respectively. Table 5 shows that higher coal/resid ratios favor the V and Ni removal from resid.

CONCLUSIONS

Hydrogenated Hondo resid (whole or 850 °F$^+$) prepared using a presulfidized NiMo/Al$_2$O$_3$ is a better coal liquefaction solvent than unhydrogenated Hondo resid. However, the asphaltenes conversion from both resid and coal to gas and oil is independent of the hydrogenation pretreatment. vanadium removal by Illinois #6 coal is dependent on the reaction time, but nickel removal is independent of the reaction time. Higher coal/resid ratios favor the V and Ni removal from resid.

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Table 1. Coal and Asphaltenes Conversions of the Coprocessing of Illinois #6 Coal with Hondo Resid and Hydrogenated Hondo Resid (Reaction Conditions: (Resid/Coal) = 2g/1g, 430 °C, 1000 psig of H_2 (cold), 1 h and 300 ppm Mo loaded to coal using $(NH_4)_2MoS_4$)

Hondo Resid	Asphaltenes Conv. % from resid and coal	Total coal conv. % for maf coal	Asphaltenes. % for maf coal	Gas + Oil % for maf coal
whole	72.5	84.3	8.3	76.0
850 °F[+]	59.6	82.9	6.4	76.5
whole (Hydro.)[a]	71.8	96.6	11.2	85.4
850 °F[+] (Hydro.)[b]	65.5	91.4	15.2	76.2

a: The hydrogenation conditions: presulfidized $NiMo/Al_2O_3$, 350 °C, 1 h, 1500 psig of H_2 (cold), and resid: catalyst = 5.5g:1g (the presulfidation was carried out at 350 °C for 2 hrs);
b: The same hydrogenation conditions as in a;

Table 2. ICP Analyses of Ni and V from the Coprocessing of Illinois #6 Coal with Hondo Resid and Hydrogenated Hondo Resid (Coprocessing Conditions: Resid/Coal = 2g/1g, 430 °C, 1000 psig of H_2 (cold) and 1h)

Reaction System	Oil		Asphaltenes		Ash/Char	
	Ni ppm	V ppm	Ni ppm	V ppm	Ni ppm	V pm
Whole resid	78	150	----	----	----	----
Hondo resid (850 °F[+])	150	290	----	----	----	----
Whole resid + Coal	*	*	150	36	1700	1200
850 °F[+] resid + Coal	*	0.62	320	150	2500	980
Hydrogenated whole resid[a] + Coal	*	*	84	19	4100	440
Hydrogenated 850 °F[+] resid[a] + Coal	*	0.45	150	53	2,100	250

a: The hydrogenation conditions: see Table 1;
*: Parameter not detected above limit of detection (Limits of detection: Ni: 2.3 ppm; V: 0.40ppm)

Table 3. Results from Catalytic Coprocessing of Illinois #6 Coal with Hondo resid (850 °F[+]) at Different Reaction Time (Reaction Conditions: Coal/Resid = 1g/2g, 430 °C, 1000 psig of H_2 (cold) and 300 ppm Mo Loaded to Coal Using $(NH_4)_2MoS_4$)

Reaction Time min	Asphaltenes conv., % (from resid and coal)	Total conv., % (for maf coal)	Asphaltenes, % (for maf coal)	Gas + Oil, % for maf coal
10	46.1	78.7	29.0	49.7
20	49.2	82.3	31.6	50.7
40	59.8	88.3	20.9	67.4
60	59.6	82.9	6.4	76.5
80	71.7	85.7	8.7	77.0
120	61.3	84.7	19.4	65.3

Table 4. Results from Catalytic Coprocessing of Illinois #6 Coal with Hondo Resid (850 °F⁺) at Different Ratios of Coal/Resid (Reaction Conditions: 1 h, 430 °C, 1000 psig of H_2 (cold) and 300 ppm Mo Loaded to Coal Using $(NH_4)_2MoS_4$)

Coal/Resid	Asphaltenes conv., % (from resid and coal)	Total conv., % (for maf coal)	Asphaltenes, % (for maf coal)	Gas + Oil, % (for maf coal)
1g/1g	64.9	93.0	4.9	88.1
1g/2g	59.6	82.9	6.4	76.5
1g/3g	55.4	70.5	25.2	45.3
1g/5g	71.6	6.0	8.4	-2.4
0.2g/1.8g	60.4	0.0	0.0	0.0
0.4g/1.6g	55.5	50.7	25.5	25.2
1.6g/0.4g	65.3	23.1	1.7	21.4
1.8g/0.2g	56.6	24.1	-3.6	20.5

Table 5. ICP Analyses of Ni and V from the Coprocessing of Illinois #6 Coal with Hondo Resid (850 °F⁺) Under Different Conditions at 430 °C, 1000 psig of H_2 (cold) and 300 ppm Mo loaded to coal using $(NH_4)_2MoS_4$

Coal/ Resid g/g	Time min.	Oil		Asphaltenes		Ash/Char	
		Ni ppm	V ppm	Ni ppm	V ppm	Ni ppm	V pm
1.0/2.0	10	*	•	370	520	310	510
1.0/2.0	20	*	65	240	450	2000	190
1.0/2.0	40	24	23	240	320	2100	610
1.0/2.0	60	*	0.6	320	150	2500	980
1.0/2.0	80	*	*	310	99	1400	1400
1.0/2.0	120	•	•	49	27	1700	1400
1.0/1.0	60	*	*	180	51	1400	820
1.0/3.0	60	*	•	310	350	710	970
1.0/5.0	60	•	*	130	120	800	980
0.2/1.8	60	*	•	240	100	8500	1500
0.4/1.6	60	*	•	130	*	1700	1500
1.6/0.4	60	*	•	•	•	420	200
1.8/0.2	60	*	*	•	*	630	120

*: Parameter not detected above limit of detection (Limits of detection: Ni: 5 ppm; V: 0.5 ppm)

SOME IMPORTANT REACTION SEQUENCES
IN THE WOMBAT PROCESS FOR CONVERTING SCRAP TIRES
TO A HIGH CARBON GEL.

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INTRODUCTION

The WOMBAT (Wertz Oxidative Molecular Bombardment at Ambient Temperature) process has been developed and refined in this laboratory over the past several years. The objective of this project is to convert scrap tires into a low polluting fuel via technology which is environmentally friendly and economically useful. The process has a high chemical oxygen demand but no external energy requirements.

RESULTS AND DISCUSSION

The WOMBAT process is initiated by introducing both the whole scrap tires and concentrated nitric acid into a closed reactor (see Figure One). Although the scrap tires are chemically inert to normal solvation processes and other types of chemical reactions using mild conditions, in the WOMBAT reactor the tires react to form a gel which is characterized by very low ash and sulfur contents. The production of greenhouse gases from combustion of the WOMBAT solid is slightly lower than that produced from typical bituminous coals.

The thermodynamic products of the WOMBAT process include steel belts (with surface corrosion), polymeric fibers, a solvent-swelled gel which may be processed into the high carbon WOMBAT solid partially described above, a solution containing several inorganic species extracted from the tires, and large quantities of $NO_x(g)$. The WOMBAT reactions appear to take place in the liquid phase, where at least three specific reaction processes occur. However, it is unclear at this time which liquid phase species present in concentrated nitric acid participate in these reactions. Consequently, in the reaction schemes presented below, HNO_3 represents a generic description of the reactants from the solution-phase nitric acid present at very high concentrations. Several of the more important reaction schemes are presented below. Although presented in a sequence, it appears that each of these (and perhaps other) reactions is occurring simultaneously in the reactor. In each of these reaction sequences, the thermodynamic products include $NO_x(g)$, and both $NO(g)$ and $NO_2(g)$ have been identified in the vapor phase within the WOMBAT reactor by FTIR. Of these, however, $NO_2(g)$ is the dominant species, while $NO(g)$ appears to occur only in trace amounts. In the discussions presented below, $NO_2(g)$ is used generically to represent the various NO_x species present in the vapor phase in the WOMBAT reactor.

The processes which occur in our reactor have a high chemical oxygen demand, as shown in Figure Two. The presence of high abundances of $NO_2(g)$ and $H^+(aq)$ in the reactor indicates that the very concentrated nitric acid, which serves as the source of the reactant(s) and also represents the principal continuing operational expense, is being comsumed in the WOMBAT process. Its escape into the atmosphere is not an environmentally acceptable process. For these two important reasons, the $NO_2(g)$ generated within the reactor, which approximates a closed adiabatic system, is catalytically recycled into reactant, as shown in the following reaction:

$$O_2(g) + 2\ NO_2(g) + 2\ H^+(aq) = 2\ HNO_3(g). \tag{1}$$
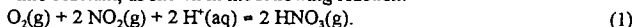
Evidence of this reaction is provided by the gas chromatographic measurements $O_2(g)$ in the WOMBAT reactor. The disappearance of the atmospheric $O_2(g)$ within the WOMBAT reactor parallels the reduction in efficiency in the WOMBAT reaction processes within the reactor. Adding either $O_2(g)$ or air to the WOMBAT reactor causes the reaction to "froth"; suggesting that the addition of $O_2(g)$, even in small amounts, invigorates the reaction by causing an *in situ* increase in the abundance of the reactant $HNO_3(g)$. Thus, the environmentally unacceptable $NO_2(g)$ is converted via an equilibrium reaction to the economically important reactant, $HNO_3(g)$.

There is no evidence of nitration reactions or of any separation of the organic species (i.e., the separation of carbon black from the styrene-butadiene co-polymer, etc.) in the gelatinous solid material which is produced by our process.

The large abundances of $NO_2(g)$ produced in the reactor are thought to be due to several distinct reaction processes which occur, at least to some extent, similtaneously. These processes include the cleavage of the metal-rubber adhesion between the brass-coated steel belts and the vulcanized styrene-butadience (**SBR**) co-polymer portion of the tire, the extensive oxidation of the vulcanized **SBR**, the extraction of the organo-sulfur from the rubbery polymer, and the acid hydrolysis of the zinc and calcium salts from the **SBR** during its conversion to a gel

$$2\ NO_2(g) + 2\ H^+(aq). \tag{2}$$

The presence of the oxidized (corroded) surfaces of the steel belts has been identified by environmental electron microscopy.

While step one is occurring, the vulcanized styrene-butadiene rubber (**SBR**) is further oxidized by a reaction scheme which may be represented as:

$$\text{SBR}(s) + n\ HNO_3(aq) \rightarrow O_n\text{--SBR}(s) + n\ NO_2(g) + n\ H^+(aq). \tag{3}$$
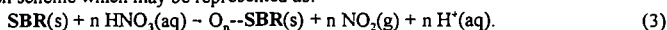
In this process, the high carbon **SBR** material (~85%) is converted from a rigidly shaped solid to a gel which has a significant oxygen content (*ca.* 13.5%) with a concomitant reduction in the carbon abundance to *ca* 73%. Mass spectral studies indicate that much of the added oxygen is in the form of carboxylates.

Accompanying the oxidation of the **SBR** is the removal of the organo-sulfur from the **SBR** the vulcanized sulfur (from 1.5% in the original styrene-butadiene impregnated rubber to *ca.* 0.7% -- or less -- in the gel). The decrease in the organo-sulfur abundance has been verified both by x-ray spectroscopy and by gas chromatography. The sulfur from the impregnated tire is converted to aqueous sulfate in the WOMBAT reactor,i.e.,

$$\text{S-R} + 4\ HNO_3(aq) \rightarrow R + SO_4^{-2}(aq) + 4\ NO_2(g) + 4\ H^+(aq). \tag{4}$$
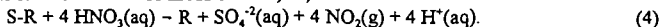
The aqueous sulfate has been precipitated from the reactor solution and then identified by x-ray diffraction and x-ray spectroscopy.

In addition, the zinc (*ca.* 2% is added in the construction of modern tires to improve their structural stability) is extracted by acid hydrolysis into the nitric acid solution during the reactor processes by an acid hydrolysis reaction such as:

$$\text{Zn} + HNO_3(aq) = ZnO_a(H_2O)_b + NO_2(g) + a\ H^+(aq). \tag{5}$$
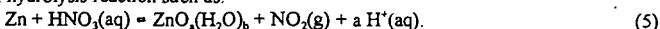
The absence of zinc in the resulting gel and its presence in the reactor solution have been verified by x-ray spectroscopy, although the specific coordination complex(es) containing the zinc have not been identified. The low ash content of the WOMBAT gel (~0.7%) is additional evidence of the successful extraction of the zinc (and other metals) from the tires. The zinc may be extracted from the WOMBAT reactor solution by chelation, as verified by x-ray spectroscopy and by x-ray diffraction, and recovered.

Some important characteristics of the WOMBAT solids are compared to several of the Argonne Premium Coals in Table I. Shown in Table II are some environmentally important fuel factors presented as ratio per million BTU's for these fuels.

CONCLUSIONS

Although the reaction schemes presented above are simplistic, taken together they account for the thermodynamic products involved in the conversion of scrap tires to useful materials.

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TABLE I. PROPERTIES OF SEVERAL SOLID STATE FUELS.

A. MEASURED FUEL VALUES

FUEL	BTU's/TON	C/TON	ASH/TON	SO_2/TON
Beulah Zap	14.9 M	1000 pds	132 pds	64 pds
Illinois # 6	22.0 M	1210 pds	285 pds	319 pds
Pittsburgh #8	26.8 M	1485 pds	182 pds	86 pds
WOMBAT	27.5 M	1083 pds	29 pds	28 pds

TABLE II. SOME IMPORTANT COMBUSTION PRODUCT RATIOS.

RATIO	FUEL			
	BZ	IL	PIT	WOMBAT
PDS CO_2/ 1 M BTU	246	201	203	196
PDS SO_2/ 1 M BTU	4.3	14.5	3.2	1.1
PDS ASH/ 1 M BTU	8.9	13.0	6.8	1.1
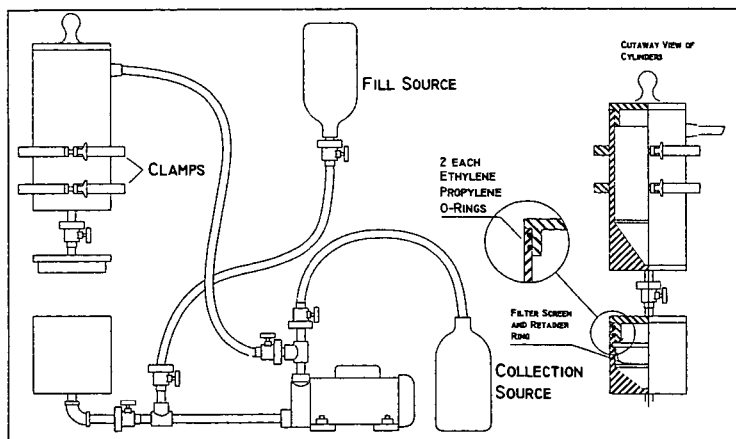
FIGURE ONE. SIMPLIFIED SCHEMATIC OF THE WOMBAT REACTOR.
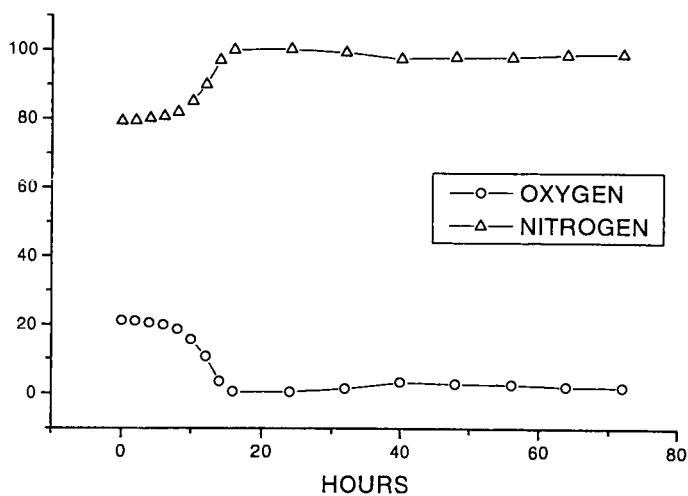
FIGURE TWO. GAS CHROMATOGRAPH OF THE OXYGEN ABUNDANCE IN THE
WOMBAT REACTOR.
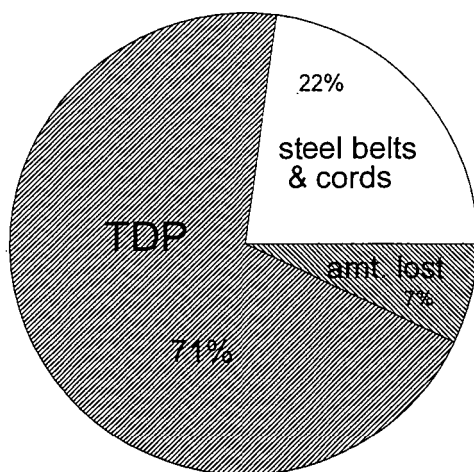
FIGURE THREE. COMPOSITION OF THE RECOVERED PARTS OF THE TIRE.